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STRENGTHENING MECHANISMS DURING THE HEAT TREATMENT OF THREE TITANIUM ALLOYS - Ti-6A1-4V, Ti-6A1-6V-2Sn, and Ti-8A1-1Mo-1V

Technical Report by

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STRENGTHENING MECHANISMS DURING THE HEAT TREATMENT OF THREE TITANIUM ALLOYS - T1-6A1-4V, T1-6A1-6Y-2Sn, and T1-8A1-1Mo-1V

ABSTRACT

The effects of solution and aging treatments on the alloys Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-8Al-1Mo-1V were investigated by hardness measurements, electron microscopy, resistance measurements at the aging temperature, and X-ray diffraction. Relatively small changes in alloy content have a marked effect on the strengths attainable by heat treatment. Two hardening mechanisms account for all the observed responses to heat treatment. These mechanisms are the decomposition of the transformed beta phase (either during the quench from the solution temperature or as the result of subsequent aging) and the precipitation of aluminum-rich α_2 in the primary alpha phase. The changes in strength as the result of heat treatment are correlated with the equilibrium alloy contents of the phases present at the solution temperature.

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INTRODUCTION

The three alloys Ti-6Al-4V (6-4), Ti-6Al-6V-2Sn (6-6-2), and Ti-8Al-1Mo-1V (8-1-1) represent popular choices of titanium alloys currently available in the United States. They differ mainly in the aluminum and vanadium contents and as will be seen the relatively small alloy changes produce considerable differences in mechanical properties as a result of solution treating and aging. In the present investigation, hardness measurements, resistance measurements at the aging temperature, and X-ray and electron microscope observations have been used to study phase transformations in the three alloys during solution and aging treatments. The strengthening mechanisms of the three alloys are compared and correlated with the compositional variations.

MATERIALS

Chemical Composition and Procedure

Experimental work was carried out on three commercial heats having the following compositions:

T1 Alloy	Al	٧	Sn	Мо	Mn	Fe	Cu	Н	0	С	N
6A1-4V	6.2	4.1	-	-	0.2	0.17	-	0.005	0.10	0.03	0.02
6A1-6V-2Sn	5.08	5.41	1.78	-	-	.55	0.66	.002	.172	.02	.02
8A1-1No-1V	7.6	1.1	-	1.1	-	.06	-	.005	.09	.022	.008

Table I. CHEMICAL ANALYSIS (Neight percent)

Specimens (approximately 1/2-inch cubes) were solution treated in air for one hour, followed by a brine quench and aged in a salt or air furnace for various times up to 32 hours, followed by a brine quench. Replica electron microscopy and standard X-ray diffraction techniques were employed to examine the polished and lightly etched specimens. Changes in resistance at the aging temperature were carried out on centerless ground specimens in an air furnace.

Phases and Their Chemical Compositions as the Result of Solution Treatment

The compositions of the phases present at various solution temperatures are listed in Table II. The compositions are based largely on the phase equilibria work of Rausch et al. and Farrar and Margolin. An absolute determination of the compositions of the phases would require a precise knowledge as to the location of the tie lines which is not available. For the purposes of the present investigation, however, only the relative changes in the compositions of the phases with solution temperature are important. The identification of the phases present in the specimens quenched from the solution temperature was ade by the use of electron microscopy and substantiated by X-ray diffraction observations. The volume fractions of the phases were determined by lineal analysis.

Table II. PHASES AND THEIR COMPOSITIONS OF T1-6A1-6V-2Sn, T1-6A1-4V, and T1-8A1-1V-1Mo AT VARIOUS SOLUTION TEMPERATURES

Solution		ion	Vol ume		cent	Weight Percent in a and/or		
	Temperature	_	Fraction*		Phase		Phase	
Alloy	(deg F)	Present	ß and/or tß	AT	٧	AT	٧	
6-4	1382	α, β	10	6	3	1	14	
6-4	1562	a, tß	25	8	2	2	8	
6-4	1742	a, tß	65	12	4	3	5	
6-6-2	1400	α, β	35	8	3 1/2	21/2	14	
6-6-2	1550	a, th, st	55	10	2	3	10	
6-6-2	1700	a, th	90	19	6	4	6	
8-1-1	1400	α, β	5	8	1	1	18	
8-1-1	1550	a, B, tBt	10	8	1	1	14	
8-1-1	1700	a, tß	20	8	1½	5	8	
8-1-1	1900	a, tß	75	16	2	6	2	

 $t\beta$ - Transformed β (martensitically)

The compositions in Table II were determined in the following manner. For the purposes of the present discussion, the 8-1-1 alloy will be considered as having effectively 2 weight percent (wt.%) vanadium (8-2). The beta phase is observed in the present investigation to be stabilized (does not transform martensitically during the quench) at a solution temperature of 1382 F in 6-4, 1400 F in 6-6-2, and 1550 F in 8-1-1. The vanadium contents in the beta phase at these temperatures is therefore taken to be 14 wt.%, since the aluminum and tin contents are not present in sufficient amounts to significantly effect the martensite transformation temperatures. The aluminum content in the alpha phases at these temperatures approaches the overall aluminum content of the alloy, except for the 6-6-2 alloy which does not contain a predominant amount of the alpha phase. Based on these observations, tie lines can be constructed on the appropriate isothermal ternary section, 1,2 and the compositions of the phases at these temperatures estimated.

The vanadium content in the beta phase for all three alloys approaches the overall vanadium content in the alloy when subjected to a solution temperature which is high in the alpha-beta region. Approximate tie lines can again be constructed and the compositions of the phases at these temperatures (1742 F - 6-4, 1700 F - 6-6-2, and 1900 F - 8-1-1) estimated. For intermediate temperatures, the vanadium contents in the beta phases were determined from a linear extrapolation of the extreme temperatures, tie lines constructed, and the compositions of the phases estimated. Of particular interest is the decrease in vanadium in the beta phase, and the increase in aluminum in the alpha phase as the solution temperature is increased up to the beta transus

^{*}Metallographic lineal analysis

[†]Trace

in all three alloys. This observation is supported in general by Williams and Blackburn⁴ for the 6-4 and 8-1-1 alloys, and some qualitative agreement based on microprobe work for the 6-4 alloy by Curtis and Spurr.⁵

THE SOLUTION-TREATED CONDITION

Figure 1 shows the effect of solution temperature on the hardness for the three alloys. While the shapes of the curves are similar, the beta transus is shifted to higher temperatures by

shifted to higher temperatures by increasing the aluminum and decreasing the vanadium contents. The relative proportions and compositions of the phases present after quenching from solution temperatures in the alpha-plus-beta region have been discussed and are presented in Table II. Specimens solution treated above the beta transus transform to martensite during the quench.

For the lower solution temperatures where the beta phase is retained during the quench from the solution temperature, there is no appreciable change in hardness in all three alloys. With increasing solution temperature, the critical temperature is reached where the beta phase begins to transform martensitically during the quench. This critical temperature occurs near the "beta-stabilized" lines which are drawn at the temperatures of minimum hardness for the alloys. While the decrease in hardness for the 8-1-1 and 6-4 alloys in this critical range is limited, the sharp drop in hardness for the 6-6-2 alloy cannot be disregard. Since it is not felt that nominal compositional

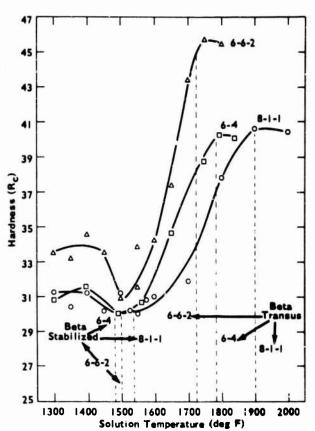


Figure I. HARDNESS VERSUS SOLUTION TEMPERATURE OF THE ALLOYS TI-6AI-6V-2Sn. Ti-6AI-4V, AND TI-8AI-1Mo-1V

changes in the phases can explain this sudden drop in hardness, it is proposed that it is due to the formation of martensite. Just why the transformation to martensite is a softening mechanism is not clear, but the transition from stable beta to martensite in specimens quenched from near the beta-stabilized temperature is supported by X-ray and electron microscope observations in all three alloys. The lower than equilibrium density observed in 6-4 for specimens quenched from a solution temperature just above the critical temperature could contribute to this softening effect.

The marked increase in hardness with increased solution temperature between the beta-stabilized and beta transus temperatures is observed for all three alloys and is accompanied by an increase in the amount of transformed beta (Table II). The hardness increase, however, is not as dependent on the quantity of transformed beta as on the extent of the decomposition of the transformed beta during the quench in a manner analogous to autotempering in steels. The decomposition products of the transformed beta are beta and alpha. That the increase in the amount of transformed beta is not sufficient to explain the increase in hardness will be seen later when the initial peak hardness during aging is observed to be far less dependent on the amount of transformed beta than would seem to be indicated in Figure 1. This initial age hardening peak, Figure 2, will be seen to be the result of the decomposition of transformed beta.

The manner in which this decomposition during the quench occurs is described in more detail elsewhere for one of the alloys, but the essential argument is briefly summarized. The M_S temperature increases not only with a decrease in vanadium content but also with an increase in aluminum content. Since the vanadium content decreases with increasing solution temperature in the alpha-beta field and aluminum content increases in the beta phase for all three alloys, the M_S temperature must also increase. The increase in hardness with increasing solution temperature is therefore explained by the ability of the specimen to more thoroughly decompose during the quench because of the higher M_S temperature.

For solution temperatures above the beta transus, the quenched hardness values are essentially constant for all three alloys. This observation reflects first of all a uniformity of microstructure which would not be expected to vary significantly as the solution temperature is changed. Since the aluminum content increases and the vanadium content changes very little in the beta phase as the solution temperature approaches the beta transus in all three alloys, the M_S temperature must increase and the decomposition of martensite should occur more readily during the quench. If this argument is correct, there should be little or no age-hardening response in these alloys which have been solution treated above the beta transus. This has, in fact, been confirmed in 6-4,6 6-6-2,8 and 8-1-1 (limited tests in this report).

THE AGED CONDITION

The effect of aging time and temperature on the hardness of specimens solution treated at various temperatures in the alpha-beta field are shown in Figures 2a, b, and c for the 6-4, 6-6-2, and 8-1-1 alloys. For each alloy, the hardness response falls into two categories; the beta phase either transforms martensitically or is retained during the quench from the solution temperature. In the former, there is a rapid initial increase in hardness with aging followed for longer aging times by secondary hardening. Apparent exceptions are observed in the 8-1-1 alloy solution treated at 1900 F and the 6-4 alloy solution treated at 1740 degrees F, where no rapid initial increase in hardness occurs with aging even though the beta phase transforms martensitically when

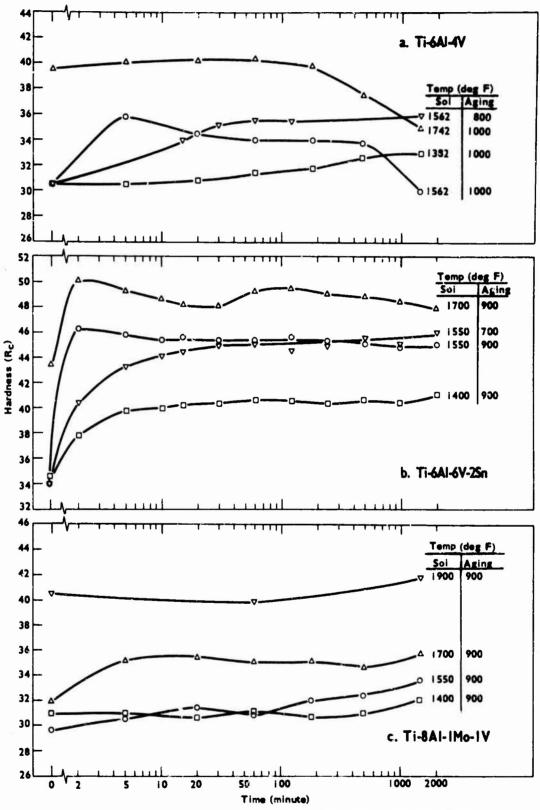


Figure 2. HARDNESS VERSUS AGING TIME FOR SPECIMENS SOLUTION TREATED AT VARIOUS TEMPERATURES

quenched from the solution temperature. As will be seen, however, the initial stage of hardening with aging is also the decomposition of martensite, and therefore the apparent inconsistency is actually due to the completion of this decomposition during the quench from the solution temperature.

When the beta phase is retained during the quench from the solution temperature, no initial rapid increase in hardness is observed with aging. A more gradual increase in hardness occurs for longer aging times. It should be noted that the designation "rapid" must be considered relative to a single alloy and not as an absolute designation, since the aging kinetics of the three alloys are not similar. The beta phase is retained only in specimens quenched from the lower solution temperatures in each alloy where the aluminum content in the alpha phase is relatively low (Table II). Since this secondary hardening is a function of the aluminum content in the alpha phase, the relatively small increases in hardness with aging in specimens quenched from these lower temperatures are expected.

The hardness observations on these alloys indicate the presence of two hardening reactions. The first is the decomposition of transformed beta to beta-plus-alpha and the second is the development of α_2 in the alpha phase.

Table III indicates some X-ray and electron microscope observations of the changes in structure of these alloys as the result of aging. In the

Table III. SOME X-RAY AND ELECTRON MICROSCOPE OBSERVATIONS OF SOLUTION TREATED AND AGED SPECIMENS

Solution Temperature	Aging	Composition						
(deg F)	Treatment	6-4	6-6-2	8-1-1				
1400	No	α, β	α, β	α, β				
1400	Yes	α, bβ	a, bß	α, β				
1550	No	a, tß	α, tβ, β*	α, β, tβ*				
1550	Yes	a, ats	α, atβ	aa, bß				
1700	No	a, tß	a, tß	a, tß				
1700	Yes	a, ats	aα, atβ	a, atß				
1800	No	tβ	tβ					
1800	Yes	atβ	atβ					
1900	No			α, tβ				
1900	Yes			α, atβ				

 $t\beta$ - Transformed β (martensitically).

aa - Aged a

bβ - Aged β

atβ - Aged transformed β

^{*}Trace

colution-treated and quenched specimens, three structures are identified, alpha, beta, and transformed beta (tB). Aging may produce three additional structures: aged alpha (aa), aged beta (bB), and aged transformed beta (atB). The aged alpha is characterized by the shift of the primary nonbasal alpha X-ray diffraction peaks toward positions of lower aluminum content. No structural changes are observed in the electron microscope. Aged beta occurs essentially instantaneously when retained beta of the right composition is heated to the aging temperature. Its formation broadens the beta X-ray diffraction line but produces no evidence of martensite formation. Structural evidence has been observed by electron microscopy in one of the alloys 5 indicating the formation of a basket-weave structure simultaneously with the broadening of the beta X-ray diffraction line. Aging the transformed beta produces a secondary beta phase richer in vanadium and a secondary alpha phase poorer in aluminum than the compositions of these phases at the solution temperature. Structural evidence for the decomposition of the transformed beta is observed in all three alloys by electron microscopy. The secondary beta phase is resolved only for aging times longer than those required to produce maximum hardness and appears to precipitate initially at the martensite-matrix interface.

Representative plots of the change in resistivity as a function of time in the aging furnace are shown in Figure 3. The magnitude of the total resistivity change (peak resistivity minus the final equilibrium resistivity, curves A, B, and D) reflects both the amount of primary alpha and its aluminum content in the solution-treated specimen (Table II). The resistivity data are related to the depletion of the primary alpha (for specimens solution treated in the alpha-beta field) of aluminum by the precipitation of α_2 . Based on this type of data, the activation energy for the process can be determined for all three alloys. The resistivity data in curves C and E, however, cannot be similarly utilized. In curve C, the equilibrium resistivity is not reached and therefore the total resistivity change is unknown. In curve E, transformations occurring in the primary beta phase during the initial minutes of aging (bß - Table III) mask the total changes in resistivity occurring in the primary alpha. It is expected that this masking effect is due to compositional changes but the details are not known.

Some values of activation energy were obtained from the raw data as shown in Figure 3 by the standard Arrhenius plot where the rate of reaction is taken as the reciprocal of the time to reach one half the total change in resistance. The values of activation energy were of the order of some 30 Kcal/g-at. for all three alloys. More extensive measurements over a wider range of aging temperatures on the 6-4 alloy gave a value of some 45 Kcal/g-at. In the present work, the calculated activation energies can be significantly increased by taking into account the resistivity changes which occur before the specimen has reached the aging temperature in the air furnace. In the case of the 6-4 and 6-6-2 alloys, activation energies in excess of 40 Kcal/g-at. have been calculated. In the 8-1-1 alloy, where the kinetics of resistivity changes are more sluggish, no quantitative assessment is justified at this time but indications are that the corrected values of activation energy would be in excess of 30 Kcal/g-at.

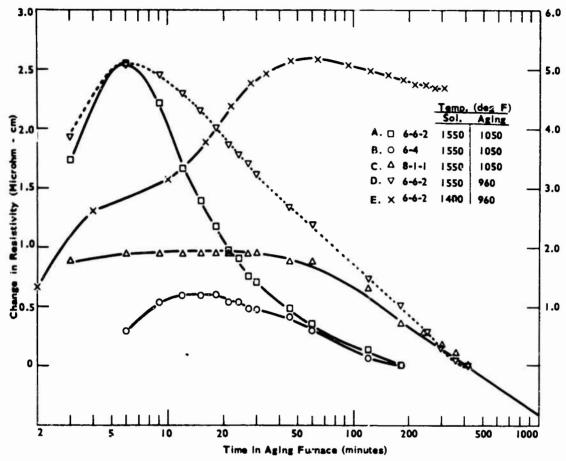


Figure 3. CHANGE IN RESISTIVITY VERSUS TIME IN THE AGING FURNACE

STRENGTHENING MECHANISMS

First Stage of Hardening

The decomposition of transformed beta to beta-plus-alpha is defined as the first stage of hardening and is the same mechanism which produces the marked increase in hardness for specimens solution treated above the beta-stabilized temperatures in Figure 1. In Figure 2 the hardness values increase rapidly during the initial minutes of aging provided the beta phase is not retained during the quench from the solution temperature. The hardness values for the 6-6-2 and 6-4 alloys show overaging for specimens solution treated at 1700 and 1562 F, respectively, but not for the 8-1-1 alloy. Metallographically this overaging is observed in all aged specimens (for sufficiently long aging times) by the appearance of precipitate preferentially at the martensite-matrix interface. The precipitates are identified by X-ray diffraction as a secondary beta phase which becomes increasingly enriched in vanadium with increased time at the aging temperature. The beta phase, of course, is developing much earlier in the aging process but could not be resolved earlier by the techniques employed.

A measure of the activation energy for the initial stage of hardening can be determined from the hardness data. In the present investigation, the values of activation energy fell in a fairly wide scatter band but never exceeded a value of about 20 Kcal/g-at. In a previous investigation, the activation energy for the decomposition of martensite in the 6-4 alloy was found to correlate well with independent data on the decomposition of martensite in the Ti-V system which had a similar vanadium content as the beta phase of the ternary. The value of 15 Kcal/g-at. determined in these investigations is far below that for normal diffusion. The decomposition of the transformed beta in these alloys is therefore felt to be controlled by vacancy diffusion.

When the beta phase is retained during the quench from the solution temperature, no rapid initial increase in hardness occurs. There is no evidence in the literature of the formation of the ω phase in these alloys for the times and temperatures used during the heat treatment in this investigation. The more sluggish increase in hardness is defined as the second stage of hardening and results from the precipitation of α_2 in the alpha phase.

Second Stage of Hardening

The existence of α_2 (Ti₃Al) for aluminum concentrations above about 5 wt.% in the TiAl system is no longer in doubt. 11-15 The precipitation of ordered α_2 particles in the 8-1-1 alloy has been observed while diffuse superlattice reflections indicating the presence of α_2 in the 6-4 alloy has been reported. 5 The precipitation of α_2 in the alpha phase in our alloys is defined as the second stage of hardening. The magnitude of the hardness increase associated with this hardening reaction is dependent both on the amount of primary alpha and its aluminum concentration in the solution-treated condition for all three alloys.

The hardness data is perhaps the most direct evidence for the second stage of hardening. Various aging response curves (secondary hardness peaks, plateaus, and even a single hardness maximum when the primary hardening mechanism is inoperative) indicate a second stage of hardening. Where the matrix phase is primary alpha, the decrease in resistivity as a function of time at the aging temperature is also associated with the formation of α_2 . While no metallographic evidence for the precipitation of α_2 was found in any of the alloys, shifts in the nonbasal alpha X-ray diffraction lines indicate a depletion of the alpha phase of aluminum.

The activation energy for the second stage of hardening has been calculated to be in excess of 40 Kcal/g-at. for the 6-6-2 and 6-4 alloys. These results seem to be in qualitative agreement with a diffusion-controlled reaction, even though the interdiffusion of solute atoms in alpha titanium has not been reported. For the 8-1-1 alloy no quantitative assessment of the activation energy has been possible except to indicate a correction which would yield an activation energy in excess of 30 Kcal/g-at. Even for 8-1-1, however, a diffusion-controlled second stage of hardening is indicated.

The difference in kinetics of the 6-6-2 and 6-4 alloys compared to the 8-1-1 alloy in Figure 3 must be due to the diffusion rates. These rates are made up of frequency and Arrhenius factors and are dependent on the solute concentrations in the titanium. While a fairly good case can be made for an enhancement of diffusion in the alpha phases of the 6-6-2 and 6-4 alloys by the presence of a third element (vanadium), the precision of the activation energy determinations from the resistivity data is not sufficient to conclude that the observed differences in kinetics are related to frequency factor effects alone. The effect of a third element would be considered in an exactly analogous way to the effect of solute atoms on the self diffusion of silver reported by Hoffman et al. 16

CONCLUSIONS

- 1. The hardness values of solution-treated specimens of these alloys is a function of the equilibrium amounts of alpha and beta phases at the solution temperature, the compositions of these phases, and the decomposition of transformed beta during the quench by a process analogous to autotempering in steels. The formation of transformed beta in itself is not a strengthening mechanism in these alloys.
- 2. Two maxima in hardness occur in all three alloys as a result of aging specimens solution treated in the alpha-plus-beta region provided the beta transforms martensitically during the quench.
- 3. The first maximum is associated with the decomposition of the transformed beta to alpha-plus-beta and is controlled by vacancy diffusion.
- 4. The second maximum is related to the precipitation of aluminum-rich α_2 and is diffusion controlled.
- 5. The observed changes in hardness which occur as the result of aging depend on the equilibrium alloy contents of the phases present at the solution temperature, primarily the aluminum content in the alpha phase and the vanadium content in the beta phase. Secondary alloying effects (aluminum in the beta phase and vanadium in the alpha phase) may explain the difference in aging kinetics between the 6-6-2 and 6-4 alloys and the 8-1-1 alloy.
- 6. Relatively small changes in alloy content of these alloys have a marked effect on both the strengths attainable by heat treatment and the kinetics of the aging response.

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INSTRUCTIONS

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